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CALCULATION OF GLASS MICROSPHERE COMPOSITIONS

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An analysis of the compositions and structural criteria of glasses for microspheres is carried out. A system of equations for modeling microsphere compositions is obtained and the applicability bounds of the model are determined. A method for developing glasses for microspheres with low hydrogen permeability and high resistance to atmospheric corrosion is proposed.

Glass microspheres are used in physical experiments as hydrogen microballoons [1]. Stringent requirements are imposed on their corrosion resistance in air and on their hydrogen permeability under ambient temperature and ambient atmospheric pressure. These requirements in effect are mutually exclusive. Chemical resistance grows with increasing content of glass-forming agents and decreasing content of modifiers, but at the same time the gas permeability grows [2 – 4], and that means that a compromise solution has to be found. The microsphere glasses have never been an object of detailed chemical engineering studies; consequently, there is no established method for developing such glasses taking into account the above requirements [5].

Note that chemical resistance is determined using the methods developed for macroglass products: window panes, container glass, etc. There are no such standard methods for microspheres; consequently, their components are selected only on the basis of general theoretical notions regarding this property. Microspheres are produced from glass batches obtained in an aqueous medium using the sol-gel method (RF patent No. 2033978) [1]; therefore, another requirement that ought to be added to the above-mentioned is the technological suitability. Liquid-phase synthesis imposes significant limitations on varying mixture compositions, since many chemicals are hardly soluble or virtually insoluble in water and, furthermore, the problem of compatibility with silicates has to be solved.

The purpose of the present study was to model vitrifying compositions for microspheres taking into account their hydrogen permeability, chemical resistance, and the technological suitability of the glass batch production.

In designing microsphere glasses, the following structural criteria *Kr* were used [5 – 9]: the silica modulus n_{Si}, the hydrogen permeability coefficient (hereafter permeability) *K*, the structure cohesion factor *Y* [8], the molar volume of the components V_i, the internal porosity P_{int}, and the structure space factor $\Sigma V_i / V_{Si}$ (ΣV_i is the total molar volume of the components without the SiO_2 volume; V_{Si} is the molar volume of SiO_2):

$$n_{Si} = \frac{C_{SiO_2}}{C_{Na_2O}};$$

$$K = 8.1 \times 10^{-14} \exp\left[-\frac{1}{T}(17{,}330 - 127.8G)\right];$$

$$Y = \frac{\sum\limits_j x_j C_j z - \sum\limits_k x_k C_k}{\sum\limits_j x_j C_j};$$

$$V_i = m_i \overline{V}_i;$$

$$P_{int} = 100\frac{V_{Si} - \sum V_i}{V_{Si}} = 100\left(1 - \frac{\sum V_i}{V_{Si}}\right),$$

where *C* is the molar content of the component, %; *T* is the temperature, K; *G* is the molar content of the glass-forming agents ($SiO_2 + B_2O_3 + P_2O_5$), %; x_j and x_k are the number of cations in the oxide; *j* and *k* are oxides containing cations with number of bonds greater than and equal to unity, respectively; *z* is the valence of the respective metal; m_i is the molar part of the oxide; $\overline{V}_i$ is the partial molar volume of the oxide, cm^3/mole.

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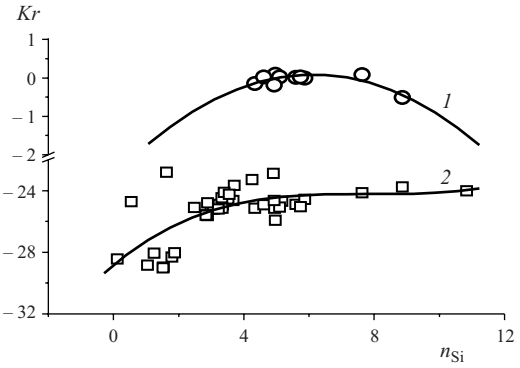

Fig. 1. Variations of the molar volume of MgO and the hydrogen permeability coefficient in vitrifying compositions: *1*) $\log V_{MgO} = f(n_{Si})$; *2*) $\log K = f(n_{Si})$.

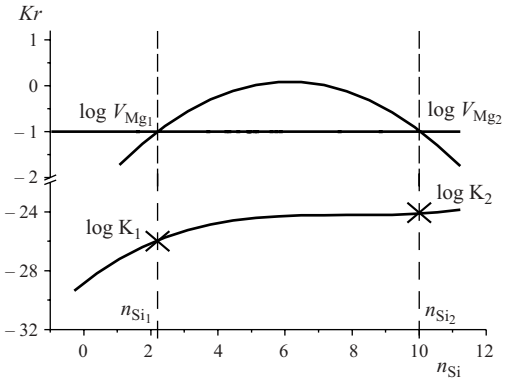

Fig. 2. An example of the ambiguous effect of MgO on hydrogen permeability depending on the silica modulus.

The silica modulus determines the ratio between the main structure-determining components (SiO_2 and Na_2O); therefore, its value can be used to predict the type of glass structure and the possibility of modifying it by introducing additional components.

We obtained sodium-silicate compositions ($n_{Si} = 1.04 – 4.90$), alkaline-borosilicate compositions with europium ($n_{Si} = 1.92 – 3.14$; RF patent No. 2033978), and lead and lead-free compositions ($n_{Si} = 2.85 – 3.67$) [1]. Certain industrially produced glasses were used for reference purposes [4, 5] (Table 1). Figures 1 – 3 show variations of the considered criteria depending on the silica modulus. The synthesized compositions, which are highly alkaline, have a low resistance to atmospheric corrosion, whereas the industrial compositions, on the contrary, have a high chemical resistance (except for the glass BaF-10). This is due to the high content of SiO_2, the application of alkaline-earth oxides RO partly replacing alkalis R_2O, the use of Al_2O_3, and a low content of B_2O_3 and R_2O, especially of K_2O.

The considered glass composition included Na_2O, K_2O, CaO, MgO, Al_2O_3, B_2O_3, SiO_2, and PbO (this composition is mostly used for chemically resistant glasses), and the need for PbO is determined by the conditions of the physical experiments.

The calculations have shown that the gas permeability may decrease with an increasing $\Sigma V_i / V_{Si}$, when the composition becomes more complex and Y decreases. The most favorable is a laminated structure. It does not make sense to strive for a structure resembling quartz glass ($Y \approx 4$), as such glass would be more resistant to atmospheric corrosion, but its gas permeability would increase [3, 4]. It is inadvisable to form a structure with $Y = 2$ [9], since the chain-structured silicates have a low chemical stability due to a high concentration of R_2O (a low modulus).

TABLE 1

Glass	Molar content in composition, %													
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	Fe_2O_3	K_2O	B_2O_3	MnO_2	SO_3	As_2O_3	PbO	BaO	ZnO
Kitaigorodskii	70.89	0.87	8.73	5.15	14.36	–	–	–	–	–	–	–	–	–
Polished (float)	72.20	0.56	9.92	5.01	12.89	–	–	–	–	–	–	–	–	–
Bottle (Industriya Works)	71.64	0.65	6.69	4.84	12.21	0.02	0.70	2.41	0.56	0.28	–	–	–	–
Crown-flint	75.10	–	2.56	–	6.93	–	8.36	1.85	–	–	0.07	5.13	–	–
Chemical laboratory No. 846	73.68	1.76	6.40	5.93	9.65	–	–	2.58	–	–	–	–	–	–
Fresnel lens	70.98	0.12	8.51	3.41	16.36	–	0.63	–	–	–	–	–	–	–
Chemical laboratory B2	73.75	2.51	9.47	–	14.27	–	–	–	–	–	–	–	–	–
Window (city of Gomel)	70.98	1.17	7.12	6.06	14.02	–	0.32	–	–	0.30	–	–	–	–
Bottle (Kalinin Moscow Works)	71.34	1.45	7.21	5.10	13.98	–	0.54	–	–	–	–	–	–	–
Light-engineering	72.11	–	5.59	5.23	15.65	–	0.64	–	–	–	–	–	0.78	–
Medical NS-1	74.75	2.71	7.68	1.53	8.44	–	1.31	3.54	–	–	–	–	–	–
Uviol	71.47	–	6.06	5.36	12.46	0.01	2.63	–	–	–	–	–	2.01	–
Headlight	73.60	0.76	7.45	3.11	14.93	–	–	–	–	–	0.15	–	–	–
Block (U.S.)	85.74	1.25	10.00	0.54	2.05	–	0.10	10.96	–	–	–	–	–	–
KF-6	73.20	1.20	–	–	21.27	–	0.65	–	–	–	–	3.68	–	–
KF-2	53.17	0.14	–	–	41.45	–	0.43	–	–	–	–	2.90	–	1.91
BaF-10	46.82	0.26	–	–	–	–	–	12.03	$2.1Mn_2O$	–	–	1.87	24.52	5.93

Depending on the silica modulus, potassium, lead, lithium, and boron oxides have an ambiguous effect on the RO structure: the curves shown in Fig. 1 are parabolas. If one constructs a perpendicular from any point on the ordinate axis (Fig. 2) and extends it to its intersection with the curves $\log V_i = f(n_{Si})$, the intersection will occur with each parabola branch, i.e., at two points. The perpendiculars drawn from these points to the abscissa axis will intersect with the curve $\log K = f(n_{Si})$ at two points as well, but with different ordinates. The shape of the curves $\log Y = f(n_{Si})$, $\log V_i/V_{Si} = f(n_{Si})$, and $\log P_{int} = f(n_{Si})$ is similar. Consequently, the same quantity of MgO, CaO, B_2O_3, Li_2O, K_2O, and Al_2O_3 under different n_{Si} values may reinforce or weaken the structure, i.e., may increase or decrease its gas permeability.

The area beneath the parabola $\log V_{Mg} = f(n_{Si})$ is the area of the intersection of the data arrays for each of the oxides considered. Therefore, they are subdivided into subarrays:

The first subarray correlates with the left branch of the curve $\log V_{Mg} = f(n_{Si})$ from $-\infty$ to the maximum:

$$\log K = -25.67464 + 1.12548X;$$

$$\log V_{Si} = 1.52843 - 0.05798X;$$

$$\log V_{Na} = 1.39377 - 1.01806X;$$

$$\log V_K = -3.28975 + 4.18119X;$$

$$\log V_{Ca} = 0.23179 + 0.04183X;$$

$$\log V_{Mg} = -0.76681 + 1.07759X;$$

$$\log V_{Al} = -5.485 + 7.42105X;$$

$$\log V_B = 1.03925 - 1.50984X;$$

$$\log V_{Pb} = 0.17588 - 0.01783X,$$

where $X = \log n_{Si}$.

The second subarray correlates with the right branch of the curve, from the maximum to $-\infty$:

$$\log n_{Si} = 1.00799 + 0.01233 \log K.$$

Note that the left branch of the $\log V_{Mg}$ parabola correlates with a decrease in the permeability (which satisfies the requirements), and the right branch correlates with increasing permeability (which should be avoided); therefore the equations for the right branch are excluded from further consideration. Using the coordinates of the intersection points of the branches of the $\log V_{Mg}$ parabola, the upper limits of the modulus ($n_{Si} \approx 5$) and the hydrogen permeability coefficient ($K \approx 1.30 \times 10^{-25}$ mole · m/(m^2 · sec · Pa)) were calculated. The lower limiti of the silica modulus was determined taking into account the data in [8] and the practical experience of the author,

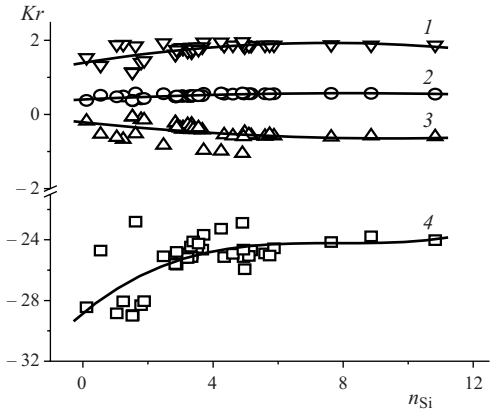

Fig. 3. Variations of the structural criteria of vitrifying compositions depending on the silica modulus: *1*) $\log P_{int} = f(n_{Si})$; *2*) $\log Y = f(n_{Si})$; *3*) $\log V_i/V_{Si} = f(n_{Si})$; *4*) $\log K = f(n_{Si})$.

and we obtain $n_{Si} \geq 2.8$; in this case the structure approaches a two-dimensional one.

An example of using the model equations for the calculation of compositions for glass microspheres. The value of the modulus was selected from the range of possible values and accepted as $n_{Si} = 5$, then $\log n_{Si} = 0.699$. Next, $\log V_i$ and V_i were calculated. The partial values were taken from [2]. Knowing V_i and $\overline{V}_i$, the molar content of the components C_i (in molar parts and in percent) were determined, which in view of the discrepancy between the preset and the calculated modulus value were refined using the correction coefficients k_{n1} and k_{n2}. Similarly, compositions with $n_{Si} = 4.0$, 4.3, 3.0, and 2.8 were calculated.

The compositions determined on the basis of a preset silica modulus equal to 5 are listed in Table 2, and the compositions calculated based on the model equations are listed in Table 3.

The following criteria were determined based on the calculated composition: $\log K = -24.8879$, $K = 8.81 \times 10^{-27}$, and $n_{Si} = 4.74$. As the preset modulus value was $n_{Si} = 5$, the correction coefficients $k_{n1} = 1.0549$ and $k_{n2} = 1.0192$ were used to refine the glass composition: $K = 8.81 \times 10^{-27}$.

Comparing the industrial and the model compositions, one can see their similarity: compositions calculated on the basis of the model equations are close to the compositions of

TABLE 2

Oxide	$\log V_i$	V_i, cm^3/mole	$\overline{V}_i$, cm^3/mole	C_i, parts	Calculation C_i, %	Refinement C_i, %
SiO_2	1.4879	30.75	27.25	1.1286	66.00	66.00
Na_2O	0.6821	4.81	20.20	0.2381	13.91	13.20
K_2O	– 0.3671	0.43	34.10	0.0126	0.74	0.77
CaO	0.2610	1.82	14.40	0.1267	7.41	7.67
MgO	– 0.0136	0.97	12.50	0.0775	4.53	4.68
Al_2O_3	– 0.2977	0.50	40.40	0.0125	0.73	0.76
B_2O_3	– 0.0161	0.96	18.50	0.0521	3.05	3.16
PbO	0.1634	1.46	23.50	0.0620	3.63	3.76

TABLE 3

Molar content in composition, %								$K \times 10^{27}$, mole · m × $(m^2 \cdot sec \cdot Pa)^{-1}$	n_{Si}
SiO_2	Na_2O	K_2O	CaO	MgO	Al_2O_3	B_2O_3	PbO		
66.00	13.20	0.77	7.67	4.68	0.76	3.16	3.76	21.0	4.74
65.20	15.16	0.39	7.50	3.92	0.24	3.89	3.70	20.0	4.10
64.54	16.14	0.29	7.38	3.57	0.15	4.28	3.65	18.0	3.82
60.93	20.32	0.08	6.72	2.44	0.01	6.10	3.40	8.3	2.90
59.82	21.36	0.06	6.57	2.21	0.01	6.64	3.33	5.1	2.72

Kitaigorodskii glass, Gomel window glass, Kalinin Works bottle glass, and Fresnel lens glass. No significant differences in the content of SiO_2, Na_2O_3, CaO, MgO, Al_2O_3, and K_2O were identified and on the average the discrepancy amounted to 7%. Considering the limited volume of data on industrial glasses resembling microsphere glasses, such divergence can be regarded as satisfactory.

A calculation of the structural parameters of the model compositions indicated that as the silica modulus increases from 3 to 5, the internal porosity grows (from 54.57 to 63.37%), the structure space factor decreases (from 0.45 to 0.37), the structure cohesion factor grows (from 3.1 to 3.24), and finally the hydrogen permeability coefficient will increase. The structure will be laminated, but with $n_{Si} > 3$, the formation of three-dimensional structural fragments is probable, which will have a negative effect on the permeability. Therefore, compositions with $n_{Si} < 5$ are preferable.

Thus, the development of compositions for microspheres (hydrogen microballoons) that have to take into account hydrogen permeability, resistance to atmospheric corrosion, and the need for synthesis in an aqueous medium includes three main aspects: analysis of structural criteria; construction of a system of equations to express the hydrogen permeability coefficient and the variation of the molar volumes occupied by the oxides in the glass structure depending on the silica modulus; and determination of the component content.

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